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Environmental Health Center
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MEMORANDUM ON THE DETERMINATION OF PHENOLS IN THE MIXED WASTE FROM A CHEMICAL MANUFACTURING PLANT

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Memorandum on the Determination of Phenols

in the Mixed Waste from a Chemical Manufacturing Plant

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At a meeting on March 22, 1949 in the offices of the National Aniline Company at Buffalo, New York, attended by representatives of the National Aniline Company; the Public Health Service; the State of New York, and the Buffalo Sewer Authority, the analytical values for phenols in a report of the Buffalo Sewer Authority were discussed. Representatives of the National Aniline Company were of the opinion that the calculated phenol contributions from the wastes given in this report were too great.

Exception was also taken to the quantity of cyanide that was attributed to the wastes from the plant. To clarify the values for cyanide and phenol, it was agreed that samples of the waste in question would be submitted to the Environmental Health Center. In accordance with this agreement, composite samples from three sources were collected by the National Aniline Company and shipped to Cincinnati for study. These samples represented:

(1) Plant "A" Effluent Sewers
(2) Plant "B" and "C" Sewers
(3) Buffalo River Water (National Aniline Intake)

Two 5-gallon carboys of each of these samples, one preserved with 1000 p.p.m. of copper sulfate, and the other preserved with 1000 p.p.m. of sulfuric acid, were received for analysis.

B.O.D., oxygen consumed, chlorine demand, and threshold taste were determined on the acid preserved samples after neutralization. Cyanides and phenols and pH were determined on the copper sulfate preserved samples. The results of the analysis of these samples were as follows:

	Plant "A"	Plant "B" & "C"	Buffalo River
5-day B.O.D.	49	415	12.0
Oxygen Consumed	255	1303	36.0
pH	6.3	6.7	6.2
One-hour Chlorine Demand	12-16	12-16	2-4
Threshold Taste (Past Breakpoint)	1/32-1/64	1/16-1/32	1/8-1/16

CYANIDE

The cyanide determinations were made according to the procedures described in the memorandum entitled "Tentative Analytical Methods for Cadmium, Chromium, and Cyanide in Water" of this Center, dated January 20, 1949. Determinations were made with both Method 1 and Method 2, (pyridine-benzidine and Liebig). No cyanide was found by either of these procedures in the wastes under study. Since the pyridine-benzidine method was sensitive to .01 p.p.m., it may be concluded that little cyanide is discharged into these sewers.

PHENOL

Phenol determinations on these samples were made by a number of methods by three different analysts during the period of April 14 to May 25, 1949. The methods used are described and the results are summarized.

METHOD I. (Standard A.P.H.A.)

To a 500 ml. sample add 0.7 ml. of 10% phosphoric acid and 0.5 ml. of 10% copper sulfate. Distill over 450 ml. and add 50 ml. of distilled water and distill another 50 ml. To aliquot portions diluted to 300 ml., add 15 ml. of borate buffer and 4.5 ml. aequeous solution of Gibbs reagent. After full color is developed, extract with 75 ml. of n-butyl alcohol, filter and make up to 60 ml. with n-butyl alcohol. Readings are made in a Bausch and Lomb spectrophotometer and compared with a 100 p.p.b. phenol standard.

METHOD II. (Alkaline Evaporation)

A 500 ml. sample is made alkaline to phenolphthalein and 400 ml. is evaporated off. The remainder is cooled and diluted to 200 ml., copper sulfate added and the sample is made acid to methyl orange with phosphoric acid and the sample is then distilled and the analysis completed as in Method I.

METHOD III. (Simple Ether Extraction)

A 500 ml. sample is made alkaline to phenolphthalein and extracted with ether. The ether layer is discarded and the remainder is acidified with HCl and extracted 3 times with ether. The combined ether layers are extracted twice with one normal sodium hydroxide. The combined caustic layers are transferred to a distilling flask and any remaining ether is boiled off. The sample is then diluted to 300 ml. with water, copper sulfate and phosphoric acid added, distilled and the analysis completed as in Method I.

METHOD IV. (Ether Extraction, I.J.C. Method)

Method IV is that procedure outlined in Analytical Methods for Boundary Waters Quality Control under Determination of Phenol.

Five hundred ml. of sample is adjusted to pH 4.0 or lower with phosphoric acid and distilled through the all-glass distilling apparatus. The distillate is acidified with phosphoric acid, 5 ml. of 10% copper sulfate added and then extracted sequentially with two 125 ml. portions of di-ethyl ether. The ether extracts, containing the phenolic compounds, are combined and extracted twice with 75 ml. portions of 0.1 N sodium hydroxide. The alkaline extract is then placed on a steam bath and heated until all the ether has been expelled. The alkaline extract is neutralized with concentrated phosphoric acid and the pH adjusted to 4.0, 5 ml. of 10% copper sulfate added, distilled and the analysis completed as in Method I.

METHOD V. (Ether Extraction Plus Salt, I.J.C.)

Method V is identical with the previously described procedure with one exception: 50 gms. of pure sodium chloride are added to the first 500 ml. distillate prior to the ether extraction to salt out the phenolic compounds into the ether layer.

The results obtained for each method are given below:

Procedure	Analyst	Date	Plant "A"	Plant "B" & "C"	Buffalo River
1. (Standard A.P.H.A.)	A	4-14	1118	4800	318
1. " "	B	5-25	1679	5396	184
2. (Alk. Evap.)	A	4-14	2536	-	133
3. (Simple Ext.)	C	4-21	1405	405	-
3. " "	A	4-14	90	135	27
4. (Ether Ext.I.J.C.)	C	4-21	239	1218	-
4. " " "	B	5-25	1066	1983	174
5. (Ether Ext.I.J.C.) (plus Salt)	B	5-25	1131	1800	171

The considerable range of results on all of these samples by the various analysts with the procedures used illustrates the frequent lack of check results that may be obtained when two laboratories report on the phenol content of such wastes. Obviously, not all of the methods previously outlined are adapted to use in this case because of the strong possibility of the presence of interfering organic compounds.

Because of the disparity revealed in the results a number of experiments were run designed to check the reliability of the various methods. The experiments conducted are outlined below with the results obtained immediately following:

Note: (Only the "A" and "B" + "C" samples were taken for analysis in the experimental work).

EXPERIMENT 1.

A 600 ml. portion of each sample (outfall "A" and "B" + "C") was distilled under acid conditions according to customary procedure. The distillate from each sample was split into two 300 ml. portions. The first portion was set up with Gibbs reagent while the second portion was further purified with ether and sodium hydroxide, using the industrial waste method as designated by I.J.C.

RESULTS IN p.p.b.

Method	Sample "A"	Sample "B" + "C"
Single Dist. Only	700	2270
Ether Ext'n. I.J.C.	390	720

EXPERIMENT 2.

A 600 ml. portion of each sample was distilled under acid condition and the distillate divided into two 300 ml. portions as in Experiment 1. Both portions were then further purified with ether, NaOH, etc., following the I.J.C. procedure.

RESULTS IN p.p.b.

	Sample "A"	Sample "B" + "C"
Sample No. 1	420	820
Sample No. 2	345	760

EXPERIMENT 3.

A 500 ml. portion of each sample was made alkaline with NaOH to pH 10+ and extracted with ether. The sample layer was drawn off, made acid with concentrated H_3PO_4, distilled and set up with Gibbs reagent. The ether layer was diluted to 250 ml. with distilled water and evaporated on a hot plate (gentle heat) until the ether had disappeared. The remaining water layer was diluted and reacted with Gibbs reagent.

RESULTS IN p.p.b.

	Sample "A"	Sample "B" + "C"
Sample Layer	230	740
Ether Layer	260	290

EXPERIMENT 4.

A 600 ml. portion of each sample was placed in a distilling flask and 250 p.p.b. of phenol added. The distillation was carried out, the distillate split into two 300 ml. portions and extracted with ether and caustic and redistilled as recommended in the I.J.C. procedure.

RESULTS

	Sample "A"	Sample "B" + "C"
1.	610 p.p.b. (-250)=360	1000 (-250)=750
2.	620 p.p.b. (-250)=370	890 (-250)=640*

(*) On Sample "B" + "C", portion 2, a part of the sample was lost when the ether was being evaporated from the caustic layer. This will undoubtedly account for the low results on this determination.

SUMMARY

	Method Single Dist.	Method Ether Extn. I.J.C.	Method Extn. from Alk.
Sample "A"	700	390 420 345 360 370	230**
Sample "B" + "C"	2270	720 820 780 750	740**

(**) Results from sample layer only reported since ether layer determination theoretically is not "phenol". Not included in the summary of results are analyses run alternately on Plant "A" and "B" + "C" by the different analysts on successive days using the Ether Extraction I.J.C. Method which follow below:

Date	Plant "A"	Plant "B" + "C"
6-29	430	950
7-1	456	1000

Results from Experiment 1 indicate that considerable material is present which is removed by the Ether Extraction Procedure. However, comparison of results from Experiments 1, 2 and 3 indicate that the non-phenolic type compounds present either are not removed quantitatively by Simple Ether Extraction or they do not react quantitatively with the Gibbs reagent.

On comparison of the results from Experiment 4 with the other extraction results obtained in Experiments 1 and 2, it would seem that phenol can be extracted and determined on a controlled added amount. Also, this experiment lends support to the belief that in spite of the presence of interfering substances in the National Aniline wastes, phenolic type compounds can be removed from the foreign materials in a quantitative manner using the Ether Extraction I.J.C. Method, although the desired accuracy is not obtained.

It should be pointed out that the phenol results obtained on this experimental series are considerably lower than the initial series of analyses. This is not surprising because of the 6 weeks interval elapsing between the time the two sets of results were obtained. However, a consistency of data is obtained when the "Ether Extraction I.J.C. Procedure" is used although as previously stated, the procedure do not give the desired accuracy or reproducibility.

More work must be done to identify the interfering substances to aid in the development of a better method of purification that will enable reliable determinations of phenol in such mixed wastes.